OBSERVATIONS ON THE RARE EARTHS: THE PURIFICATION AND ATOMIC WEIGHT OF SAMARIUM

BY

ALBERT WAFFLE OWENS

B.S. Bucknell University, 1909.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

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ACKNOWLEDGMENT.

This work was begun in the fall of 1911, at the suggestion of Professor C. W. Balke. The first part of the problem, the purification of the rare earth material, was carried out entirely under his supervision, as were also the preliminary atomic weight determinations. The final determinations, by both ratios, were made under the supervision of Dr. B. S. Hopkins and Dr. H. C. Kremers.

The author wishes to acknowledge his indebtedness to the above mentioned persons for the interest they have shown and the many helpful suggestions they have given during the course of this investigation.

OBSERVATIONS ON THE RARE EARTHS: THE PURIFICATION AND ATOMIC WEIGHT OF SAMARIUM.

Introduction.

This investigation was undertaken as a part of a general program mapped out in 1911 for work on the purification and atomic weights of the different rare earth elements. The samarium material was purified to a high degree preliminary to the determination of its atomic weight. The ratios oxide to chloride, and oxide to chloride hydrate, were found to be unsatisfactory and were replaced by the ratio chloride to silver.

Historical.

The atomic weight determinations made on samarium material from the time of its discovery in 1878 by Delafontine,[1] are listed in the following table along with the investigators and the ratios used:

TABLE I.

Date.	Investigator.	Ratio.	Atomic weight.
1880	Marignac[2]	Unknown	149.4
1881	Delafontine[3]	Unknown	151.5
1883	Cleve[4]	Oxide-sulfate	150.02
1891	Bettendorf[5]	Oxide-sulfate	150.46
1900	Demarcay[6]	Oxide-sulfate	148.0
1904	Käppel[7]	Hydrated sulfate-oxide	151.59
1904	Urbain and Lacomb[8]	Hydrated-anhydrous sulfate	150.34
		Anhydrous sulfate-oxide	150.346
		Hydrated sulfate-oxide	150.346
1905	Matignon[9]	Anhydrous-basic sulfate (Sa_2SO_6)	150.6
1906	Feit and Przibylla[10]	Volumetric	150.47
1917	Stewart and James[11]	Chloride-silver	150.44

Purification of Reagents.

Water.—The ordinary distilled water was redistilled from alkaline permanganate, in the block-tin still used in this laboratory for the prepara-

[1] *Compt. rend.*, **87**, 632 (1878).
[2] *Arch. sci. phys. nat.*, [3] **3**, 435 (1880).
[3] *Compt. rend.*, **93**, 63 (1881).
[4] *Chem. News*, **48**, 39 (1883).
[5] *Am. Chem. Pharm.*, **263**, 164 (1891).
[6] *Compt. rend.*, **130**, 1185 (1900).
[7] *Ann.*, **331**, 16 (1904).
[8] *Compt. rend.*, **138** (1904).
[9] *Ibid.*, **141**, 1230 (1905).
[10] *Z. anorg. Chem.*, **50**, 249 (1906).
[11] *J. Am. Chem. Soc.*, **39**, 2605 (1917).

tion of "conductivity" water. By the most sensitive nephelometric test this water gave no test for chlorides.

Oxalic Acid.—C. P. oxalic acid was twice recrystallized from conductivity water acidified with nitric acid, and once from conductivity water alone. The solutions were evaporated to saturation and then were violently agitated while being rapidly cooled. This gave very fine crystals which could be well drained by suction and practically dried in a porcelain bowl centrifuge. The crystals were then air-dried for preservation. The acid thus prepared gave no residue on igniting a 20 g. sample.

Nitric Acid.—C. P. nitric acid was distilled from a quartz distilling flask directly into a quartz receiving flask and preserved in the latter. The first third and the last third were discarded but the middle third was saved for use. This acid gave no test for chlorides.

Hydrochloric Acid.—C. P. hydrochloric acid was heated in a quartz distilling flask and the hydrogen chloride was absorbed in conductivity water in a quartz receiving flask. The acid was purified at frequent intervals and was kept in the receiving flask.

Hydrogen Chloride—Previously heated C. P. sulfuric acid was dropped into C. P. hydrochloric acid and the gas thus formed conducted through the drying towers. These two towers were one meter high by twenty-five millimeters in diameter, and were filled with glass beads moistened with previously boiled sulfuric acid. All connections in this apparatus were either of sealed glass or of dry ground glass.

Nitrogen.—Air, from the compressed air system, was forced through concentrated sulfuric acid and glass wool to remove any dust. The oxygen was removed by bubbling the dust-free air through a wash bottle filled with concentrated ammonia, and was passed through an electrically heated quartz tube containing a roll of copper gauze. The nitrogen thus obtained was purified by passing it through a train of vertical glass towers sixty centimeters high and two and one-half centimeters in diameter. Where liquid reagents were used, these towers were filled with glass beads and a dropping funnel was sealed into the top so that the various liquids could be dropped onto the beads without admitting air into the system. In the first tower the glass beads were moistened with dilute sulfuric acid to remove the excess of ammonia. In the second tower the glass beads were moistened with a saturated solution of silver sulfate to remove any arsine, hydrogen sulfide, or the like. In the third and fifth towers the glass beads were moistened with previously boiled sulfuric acid to remove most of the water. The fourth tower contained broken sticks of fused potassium hydroxide to remove moisture and carbon dioxide, and was sixty centimeters in height by four centimeters in diameter. The sixth and last tower contained glass wool into which phosphorus pentoxide

had been freshly sublimed. This was to remove the last traces of moisture.

Air.—The air was purified by passing it through a red hot quartz tube filled with platinized quartz and then through a purifying train similar to the one used for nitrogen. The beads in the first tower, in this case, were moistened with dilute sodium hydroxide in order to remove the carbon dioxide, for it was found that the solid potassium hydroxide would not remove all of this impurity.

The trains for purifying the different gases were all mounted on a single wooden frame in as compact a form as possible. All connections in the apparatus were either of sealed glass or of ground glass. By means of two "Y" tubes and three glass stopcocks any one gas or any mixture of the three gases could be delivered into the reaction flask. This type of drying apparatus was first used by Balke and Egan[1] in their determination of the atomic weight of yttrium.

Silver.—The silver used in these determinations was very kindly donated by Dr. H. C. Kremers. It was a part of a quantity which he had prepared for like atomic weight determinations and its preparation has been previously described by him.[2]

Preparation of Pure Samarium Oxide and Chloride.

(*a*) **Separation of Samarium from Lanthanum, Praseodymium and Neodymium.**—The source of the material used in obtaining the pure samarium material was some 400 pounds of cerium-earth double sulfates from the Welsbach Mantle Co. These sulfates contained all of the members of the cerium group, but as the original source of the material was monazite sand there was very little europium or gadolinium present. Most of the cerium had been removed for commercial purposes and the yttrium earths had been roughly removed by precipitating out the cerium earths as double sulfates with a saturated solution of sodium sulfate.

The double sulfates were boiled with a strong solution of sodium hydroxide until they were completely decomposed. The solution was diluted and the hydroxides were washed with boiling water until they were free from sulfates. In order to remove the remaining cerium, the hydroxides were dissolved in nitric acid, the solution was made nearly neutral, heated to boiling and potassium bromate added. As the red fumes of bromine appeared, marble dust was added to keep the solution nearly neutral and the solution was boiled until some of the filtered liquid failed to give a test for cerium with hydrogen peroxide. The small amount of cerium basic nitrate and the excess marble were filtered off. The rare earth oxalates from this solution were ignited to oxides and these were

[1] *J. Am. Chem. Soc.*, 35, 365 (1913).

[2] *Ibid.*, 40, 602 (1918).

dissolved in dil. nitric acid. In order to convert these nitrates into the magnesium earth double nitrates for fractionation, as first recommended by Demarcay,[1] a quantity of nitric acid equal to the amount used in the solution of the oxides was neutralized with magnesium oxide, and the two solutions filtered and united. This solution was then fractionally crystallized for the separation of the samarium material. When the most soluble fractions, containing the bulk of the samarium, began to crystallize poorly, they were diluted, filtered, and the earths precipitated as oxalates in order to remove any impurites of the common elements which might be present.

When no more samarium appeared at the soluble end the fractionation was discontinued. The samarium oxalate was ignited, and the oxide was again converted into the magnesium samarium double nitrate as described above. In the second series of fractionations the most soluble fractions were set aside when no more absorption lines of neodymium were visible through 10 cm. of a saturated solution.

(*b*) **Separation of Samarium from Europium and Gadolinium.**—The material from the previous fractionation now contained some europium and gadolinium and possibly a very small amount of yttrium earths. After the yttrium earth nitrates had been removed, by running the samarium magnesium double nitrates through about 180 fractionations with 30% nitric acid, bismuth magnesium double nitrate was added at the soluble end. According to Urbain and Lacomb,[2] the bismuth magnesium double nitrate crystallizes between samarium and europium with gadolinium still more soluble than europium. After about 40 crystallizations of this series the first 6 determinations were made. Before making any further determinations it was thought advisable to fractionate the bismuth and samarium double nitrates still more, even though for some time the material had shown no other adsorption lines than those of samarium. The material was put through about 150 more crystallizations before the final series of oxide-chloride determinations were made. The samarium chloride-silver determinations were made with the very best material.

(*c*) **Conversion into Oxide.**—The samarium material used for the atomic weight determinations was taken from the middle series of the samarium bismuth magnesium nitrates described above. The nitrates were thoroughly fused in a porcelain dish and the oxides and basic nitrates thus formed were dissolved in as little hydrochloric acid as possible. After evaporating this solution to a syrupy condition, it was poured into a large volume of distilled water. The bismuth oxychloride was allowed to settle and the supernatant liquid siphoned off. The cold solution containing

[1] *Compt. rend.*, 130, 1019 (1900).

[2] *Ibid.*, 137, 793 (1903).

the samarium chloride and magnesium chloride was saturated with hydrogen sulfide in a 10-liter flask, and was then digested on the steam bath until the brown coloration entirely disappeared and the bismuth sulfide settled out. The bismuth sulfide was filtered off and the solution again saturated with hydrogen sulfide. This was repeated until no further precipitation of bismuth sulfide was obtained. The hydrogen sulfide was removed by forcing filtered air through the boiling solution. The solution was made 1% acid with nitric acid and samarium oxalate precipitated out with hot dil. oxalic acid.

In precipitating samarium oxalate it was found best to do so from a boiling 1% nitric acid solution, using a boiling solution of dil. oxalic acid as the precipitant. By adding the oxalic acid until the precipitate first formed, just failed to redissolve and then cooling the solution rapidly, it was found possible to obtain a very fine precipitate which was crystalline, settled rapidly, and washed well on a Büchner funnel. These oxalates were dried and ignited in platinum dishes in an electric oven in order to convert them into oxides. The oxides were then dissolved in nitric acid and the samarium precipitated as hydroxide by passing ammonia vapors into the flask while the solution was being agitated. The hydroxides were washed by decantation until they started to become colloidal and were then washed on a Büchner funnel. The oxalate and hydroxide precipitations were carried out alternately, 3 times for each sample. The oxalates were ignited at 800° for 6 hours and then at 900° for 2 hours. In this way it was hoped that all the carbonate first formed would be decomposed to the oxide.

(*d*) **Conversion into Anhydrous Chloride.**—The method of converting samarium oxide into anhydrous chloride was somewhat similar to that used by Baxter in preparing other rare earth chlorides. Instead of the bottling apparatus used by the latter, a quartz reaction flask, first described by Egan,[1] was used to obtain the transformation. This had the advantage that the oxide was changed to chloride in the apparatus in which it was weighed and the chloride was also weighed in the same apparatus.

The samarium oxide, ignited as described above, was transferred to the previously weighed reaction flask while still hot, and the outlet and inlet tubes were inserted and their air-tight caps were adjusted. The reaction flask was then placed in a desiccator and the latter placed in the balance room for one hour. After loosening one of the caps to equalize the pressure, the flask was hung in the balance case and weighed at intervals of $^1/_2$ hour until it had come to equilibrium

All weighings were made on a very sensitive Ruprecht balance used exclusively for atomic weight work, in a special cork-lined room, the tem-

[1] *J. Am. Chem. Soc.*, 35, 365 (1913).

perature of which seldom varied more than 3°. All weighings were made by substitution, using a similar flask as tare. The weights were either of platinum or of gold-plated brass and were calibrated to 0.01 mg. All weights were corrected to vacuum before being used in any calculation. The specific gravity of the brass weights was taken as 8.4, of the platinum weights as 21.5, of the samarium oxide as 8.247,[1] of samarium chloride as 4.465,[2] of samarium chloride hydrate as 2.383,[3] and of silver as 10.53. The atomic weights were taken as follows: oxygen, 16.0; chlorine, 35.46; silver, 107.88; and hydrogen, 1.008.

The oxide in the flask was moistened with water and then dissolved in pure hydrochloric acid. The oxide always dissolved to a clear amber-colored solution without any apparent effervescence or spattering. The reaction flask was then attached to the drying train by means of the two ground joints and enclosed in an electrically heated oven having glass sides through which the progress of the dehydration could be watched. This oven also protected the flask from the fumes of the laboratory during the time it was connected to the train. The oven was heated to 130°, and a brisk stream of air was passed through the flask thus driving off most of the excess water. The temperature was then dropped to 105°, and hydrogen chloride, passed in to cause the formation of samarium chloride hydrate, as this procedure allowed the excess solution to creep up the sides of the flask, and exposed a larger surface for dehydration. The first 5 molecules of water were removed below 105°, by a current of air and hydrogen chloride, in from 10 to 12 hours. This point was shown by the absence of moisture in the cooler portions of the exit tube. The proportion of hydrogen chloride was now increased and the temperature was gradually raised to 190° where the last molecule of water was expelled. Hydrogen chloride alone was now passed through the flask and the temperature gradually raised to 360°, where it was held for one hour. The oven was then removed, the stream of hydrogen chloride was stopped, and the samarium chloride was fused either with a Bunsen flame or with an electric pot furnace. There was no evidence that the samarium chloride was appreciably volatile at its melting point. According to Matignon,[4] anhydrous samarium chloride melts at 686°. When free from oxychloride the samarium chloride melts to a reddish liquid which does not wet the bottom of the quartz flask. If, however, any oxychloride is present the melt wets the flask, attacks it, and fuses with much more difficulty. After the samarium chloride was fused the flask was cooled in an atmosphere of hydrogen chloride and then air was passed through the flask until all

[1] *Chem. News*, 51, 145 (1885).
[2] *Compt. rend.*, 140, 1339 (1905).
[3] *Chem. News*, 53, 45 (1886).
[4] *Compt. rend.*, 141, 1230 (1905).

traces of hydrogen chloride were removed. By first adjusting the cap on the outlet tube, and then the one on the inlet tube, the flask could be sealed without admitting any undried air. The samarium chloride was weighed in a manner similar to that described for the oxide.

At first nitrogen was used in the early part of the dehydration, but this was found to be unnecessary. Furthermore, it was found that samarium chloride heated for some time in a current of nitrogen lost chlorine, and was reduced to samarous chloride ($SaCl_2$). According to Baxter, nitrogen prepared in this way contains some hydrogen and these experiments seem to confirm his statement for tests showed that hydrogen chloride was given off and not chlorine. The samarous chloride was a purplish brown crystalline mass and had the other properties ascribed to it by Matigon.[1] The use of nitrogen was discontinued, because of the danger of reducing the samaric chloride.

All the samples of samarium chloride dissolved completely in cold water. In order to test the hydrogen ion concentration of the samarium chloride solution, samples from a preliminary run were treated with the following indicators: rosolic acid gave yellowish pink; methyl orange gave yellow; congo red gave orange; phenolphthalein gave a colorless solution; and litmus gave red-violet. These results, according to Washburn, indicate a hydrogen ion concentration of about 10^{-8}.

The Ratio of Samarium Oxide to Samarium Chloride.

In about 1911 Prof. C. W. Balke and his associates began a series of atomic weight determinations on various elements of the rare earth family. As a few preliminary experiments showed that the oxide-sulfate and hydrated sulfate ratios were unreliable they decided to use the oxide-chloride ratio. Egan,[2] Sears,[3] Engle,[4] Hopkins,[5] Kremers,[6] and Wichers.[7] have used this ratio for atomic weight determinations.

The first 6 determinations were made in 1913 with material from the middle of the best series. Although this material showed no other absorption spectra than that of samarium, one year was spent in making further fractionations from nitric acid of 1.30 sp. gr. As the results from the next 8 determinations were in no better agreement than those from the first 6, it was decided to obtain the oxide from different sources. Dr. Kremers found that the oxide chloride ratio gave consistently higher results than the chloride silver ratio in the determination of the atomic

[1] *Loc. cit.*
[2] *Ibid.*
[3] *J. Am. Chem. Soc.*, **35**, 833 (1913).
[4] *Ibid.*, **39**, 53 (1917).
[5] *Ibid.*, **38**, 2332 (1916).
[6] *Loc. cit.*
[7] *J. Am. Chem. Soc.*, **40**, 1615 (1918).

weight of dysprosium. Dr. Wichers found that it was impossible to prepare pure erbium oxide by the ignition of the oxalate. Samarium nitrate and samarium hydroxide were, therefore, used as the source of oxide in the next 8 determinations. These samples were ignited at 900° and then ground in an agate mortar, the process being repeated 3 times in order to obtain as pure an oxide as possible. These results were no better than the previous ones so this ratio was abandoned because of the difficulty of obtaining pure samarium oxide. The results of these determinations are shown in Table II.

TABLE II.—THE RATIO OF SAMARIUM OXIDE TO SAMARIUM CHLORIDE.

No.	Fraction.	Sm_2O_3.	$SmCl_3$.	$\frac{Sm_2O_3}{2SmCl_3}$	Atomic weight.
1	"Y" 9	2.02880	2.96071	0.685241	155.35
2	10	1.93168	1.82413	0.681926	154.32
3	11	2.14582	3.14583	0.681925	152.64
4	12	1.87697	2.75032	0.682450	153.06
5	13	2.10497	3.08696	0.681891	152.60
6	14	2.00366	2.93206	0.683362	153.81
7	"B" 32	1.94568	2.86280	0.679642	150.77
8	33	1.40475	2.06003	0.681907	152.61
9	34	1.41450	2.06679	0.684395	154.60
10	35	1.74706	2.55834	0.682888	153.42
11	36	2.24454	3.29615	0.680958	151.85
12	37	1.76129	2.58650	0.680944	151.83
13	38	2.89804	4.25958	0.680270	151.28
14	39	4.28692	6.29651	0.690840	151.75
15	40	4.44327	6.49606	0.683979	154.30
16	40	5.63415	6.82623	0.678859	150.15
17	41	3.94926	5.78425	0.682761	153.30
18	41	3.94868	5.78354	0.682763	153.31
19	42	4.42173	6.47502	0.682890	153.43
20	42	2.76538	4.03877	0.684784	154.95
21	43	2.96307	4.25295	0.696709	160.00
22	43	2.97545	4.34537	0.684740	154.94

Preparation of Samarium Chloride Hexa-hydrate.

The purest oxide was dissolved in freshly prepared hydrochloric acid and the solution was filtered through a washed, hard, filter paper. This solution was evaporated, under cover, until crystals began to form on the surface, and was then cooled in iced brine, and stirred until cold. This procedure gave small crystals which were easily dried in a high-speed centrifuge. These crystallizations were repeated five times to insure the removal of the more common elements whose chlorides do not crystallize isomorphously with those of the rare earths. No change in the atomic weight was noticeable in the determinations made with this specially purified material.

The Ratio Samarium Chloride Hexa-hydrate to Samarium Chloride.

The purest samarium chloride, hexa-hydrate, was placed in the reaction flask and dry air passed over it at 27° C. Weighings were made every hour to determine the rate of loss of water. In this way it was hoped that the exact point could be determined when the hexa-hydrate was reached. It was found, however, that the hexa-hydrate when exposed to dry air at 27° would lose water continually, and finally lose its crystalline structure, and fall to a powder. No attempt was made to determine whether there were any intermediate hydrates between the hexa-hydrate and the mono-hydrate. The weight of the air-dried crystals was compared to the weight of the anhydrous salt in order to determine the atomic weight. The results are of no significance, as far as the atomic weight is concerned, but are given in the following table as a matter of interest:

TABLE III.—THE RATIO OF SAMARIUM CHLORIDE HEXA-HYDRATE TO SAMARIUM CHLORIDE.

$SmCl_3.6H_2O$.	$SmCl_3$.	$\frac{SmCl_3}{SmCl_3.6H_2O}$	Atomic weight.
4.01787	2.81639	0.700966	145.92
4.46239	3.13555	0.702648	149.03
4.04032	2.91019	0.702289	148.58
5.92563	4.15775	0.701655	147.79
4.73448	3.32505	0.702305	148.60
2.98049	2.08632	0.700000	145.72

The Ratio Samarium Chloride to Silver.

The ratio of a rare earth chloride to silver was first used by Baxter and Chapin[1] to determine the atomic weight of neodymium and was later used by Baxter and Stewart[2] to determine the atomic weight of praseodymium. Stewart and James[3] also used this ratio in their revision of the atomic weight of samarium.[4] Egan tried to use this ratio in his determination of the atomic weights of yttrium, but for some unknown reason he failed to get concordant results. The ratio was not used again in this laboratory until it was successfully carried out by Kremers in his determination of the atomic weight of dysprosium.

In order to become familiar with the manipulations necessary in this ratio, a few determinations of pure fused sodium chloride against silver

[1] *J Am. Chem. Soc.*, 33, 1 (1911).

[2] *Ibid.*, 37, 516 (1915).

[3] *Ibid.*, 39, 2605(1917).

[4] At the time Stewart and James published their article entitled, *A Revision of the Atomic Weight of Samarium*, the laboratory work on the present investigation was nearly completed. the first thirteen determinations having been finished. Due to the stress of the times these results could not be published sooner.

were made. The results were quite comparable to those of Richards and Wells for the same ratio.

The anhydrous samarium chloride was weighed in the reaction flask, in which it had been dehydrated, and was dissolved in conductivity water. The solution was quantitatively transferred to a 1.5 liter glass-stoppered Jena Erlenmeyer flask, and diluted to 400 cc. Assuming the atomic weight of samarium to be 151.0, within a few tenths of a milligram of the calculated weight of silver was weighed out, and dissolved in dil. redistilled nitric acid in a liter Jena Erlenmeyer flask fitted with a column of bulbs, 50 cm. high, to retain any spray. The silver nitrate solution was diluted to 400 cc. and added gradually to the dilute samarium chloride solution while the latter was being violently agitated. After agitating for 3 hours in a motor-driven shaking machine, the solution was allowed to stand for 12 hours, and the clear supernatant liquid was then tested in a nephelometer for an excess of either chlorine or silver. All work which involved materials affected by light was done in a dark room. After testing the supernatant liquid, portions of standard silver nitrate or sodium chloride solutions were added from weighing pipets until exact equivalence was reached. The amount of silver used, as silver nitrate, was added to the amount originally weighed out, and the silver equivalent of the sodium chloride added was subtracted from the total silver. It was necessary to add sodium chloride when too much silver had been weighed

TABLE IV.—THE RATIO OF SAMARIUM CHLORIDE TO SILVER.

No.	Fraction.	$SaCl_3$.	Ag weighed out.	Ag added.	Ag total.	$\frac{SaCl_3}{3\,Ag}$.	Atomic weight.	
1	42	6.47502	8.14202	+0.01608	8.15810	0.793692	150.49	
2	42	4.03877	5.09024	—0.00941	5.08083	0.794903	150.90	(SaOCl)
3	43	4.25295	5.36673	—0.00745	5.35928	0.793567	150.45	
4	43	4.34537	5.47543	+0.00120	5.47663	0.793442	150.41	
5	44	3.84046	4.74751	+0.09251	4.84002	0.793480	150.42	
6	45	3.32317	4.31449	—0.12629	4.18820	0.793460	150.42	
7	32	2.96369	3.73081	+0.00423	3.73504	0.793480	150.42	
8	33	3.34818	4.21583	+0.00353	4.21936	0.793527	150.44	
9	34	3.27999	4.13128	+0.00205	4.13333	0.793546	150.44	
10	35	3.00394	3.78617	+0.00152	3.78769	0.793396	150.40	
11	36	2.36481	2.97873	+0.00097	2.97970	0.793640	150.47	
12	37	3.68616	4.64535	+0.00042	4.64577	0.793444	150.41	
13	38	3.17435	4.00033	—0.00013	4.00020	0.793548	150.44	
14	39	2.81639	3.54905	+0.00027	3.54932	0.793501	150.43	
15	40	3.13555	3.95087	+0.00068	3.95155	0.793500	150.43	
16	41	2.91019	3.66900	—0.00154	3.66744	0.793520	150.44	
17	42	4.15775	5.23920	+0.00053	5.23973	0.793504	150.43	
18	43	3.32505	4.18985	—0.00033	4.18952	0.793650	150.47	
19	44	2.06632	2.62794	+0.00156	2.62950	0.793430	150.41	

Omitting No. 2, because SaOCl was known to be present, average = 150.43

out, or when too much silver nitrate had been added. After each addition the flask was shaken for 2 hours and was then allowed to stand from 8 to 12 hours before testing again.

The samarium chloride for determinations 1–4 was obtained from the last 4 determinations of the oxide-chloride ratio. In determinations 5–13 the anhydrous chloride was obtained by introducing a saturated solution of samarium chloride into the flask and dehydrating as described above. In determinations 14–19 the anhydrous chloride was obtained from the determinations of the ratio hydrated chloride to anhydrous chloride. Although the material for these last 6 determinations was purified more than the previous material, the atomic weights are virtually the same.

The results of this ratio are shown in Table IV.

Summary.

1. Samarium material was obtained from rare earth residues purchased from the Welsbach Mantle Co. The cerium was removed by means of bromine and marble. Lanthanum, praseodymium and neodymium were removed by fractionation of the rare earth magnesium double nitrates, first from a water solution and then from nitric acid of 1.30 sp. gr. Europium and gadolinium were removed by fractionation of the rare earth magnesium double nitrates along with bismuth magnesium double nitrate. The final purification was the alternate precipitation of samarium material as hydroxide and oxalate and 5 recrystallizations of this material as hydrated chloride.

2. The oxide-chloride ratio was found unsatisfactory due to the difficulty of obtaining pure oxide. Oxide was obtained by igniting the oxalate, nitrate and hydroxide, but the results were equally discordant.

3. The hydrated chloride-anhydrous chloride ratio was found unsatisfactory due to the difficulty of obtaining pure samarium chloride hexahydrate.

4. The anhydrous chloride-silver ratio was altogether satisfactory and these values are to be taken in preference to all others.

5. The results of this investigation confirm the results of Stewart and James as to the value of the atomic weight of samarium.

VITA.

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